

Surface Treatments of Fillers to Improve Dielectric Coatings

Lee M. Kindley
Melpar, Inc.

I. Introduction

The inability of present dielectric coatings to meet stringent reliability requirements under adverse moisture conditions and broad temperature ranges is one of the major problems facing the electronics industry. Each major class of dielectric material, organic and inorganic, has obvious advantages and disadvantages for use in dielectric coatings. Unfortunately, combinations of these classes usually do not produce coatings which are significantly better than those obtainable with either class of material alone.

We, at Melpar, have proposed that to obtain significant improvement in the composite properties of the two classes of dielectrics, improvement at the inorganic-organic interface must be accomplished. To do this we have proposed treatments of the filler surface to enhance the bonding characteristics of the inorganic and organic systems.

II. Discussion of Problem

The interface between the surface of inorganic fillers and organic resin binders in coatings provides sites for water absorption and a route for water vapor transmission. It seems logical to assume that there would be less opportunity for moisture to penetrate along the interface if the organic binder adhered to or "wet" the surface of the filler particle. We have theorized that the stronger the adherence, the more impermeable and moisture resistant the coating will be. The ultimate in adherence between the two classes of material should result from actual chemical bonding between the surfaces.

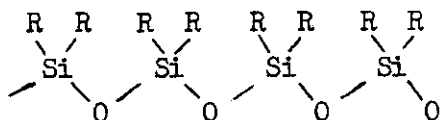
Two basically different conditions for surface treatment of inorganic fillers were considered in attempting to attain greater adhesion between filler particles and resin binder.

Under one condition, it was assumed that the filler particles had small amounts of moisture or other contaminating molecules on the surface. These contaminants (especially moisture) present a barrier which prevents the organic binder from making close contact with the surface of the filler. Adhesion is thereby reduced and a condition favoring permeability along the interface is afforded. Numerous examples may be cited which prove that the presence of absorbed impurities on solid surfaces reduces the adhesion of liquids to that surface.

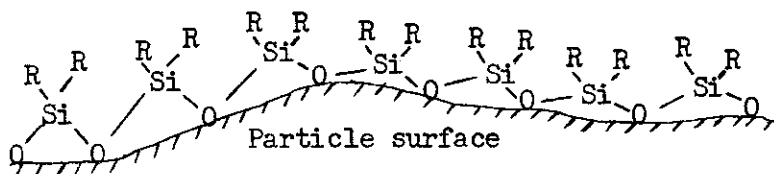
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Under the second condition it was assumed that the surfaces of the filler particles were free from adsorbed molecules or that the contaminants had been removed. Under these conditions, adhesion between the filler particle surface and the organic binder are most favorable. Still, there are strong repelling forces which tend to prevent close contact between the polar surface of most filler materials and the non-polar organic binder. It seemed that under such conditions a strong bond might be effected by introducing a third component-one which contained both polar and non-polar groups. Molecules of this type might be able to align themselves in such a way that one end would react at the surface of the filler particles and the other end would react with the organic binder. By such a mechanism a strong union of filler and binder could be realized.

This idea has been successfully exploited in a number of similar applications. For example, the treatment of inorganic fillers used in rubber coatings with particular dihydrocarbon-substituted silicones has resulted in considerable improvements in thermal stability and impermeability in some of the coatings tested. The concept of the "silicone bridge" has been used to account for the improvement in physical properties. According to this concept, the highly polar Si-O bond sets up forces of attraction which materially affect the oriented configuration of the silicone chain in relation to filler surfaces. The dihydrocarbon-substituted polymeric siloxane molecule when subjected to orientation forces may be formally represented as follows:

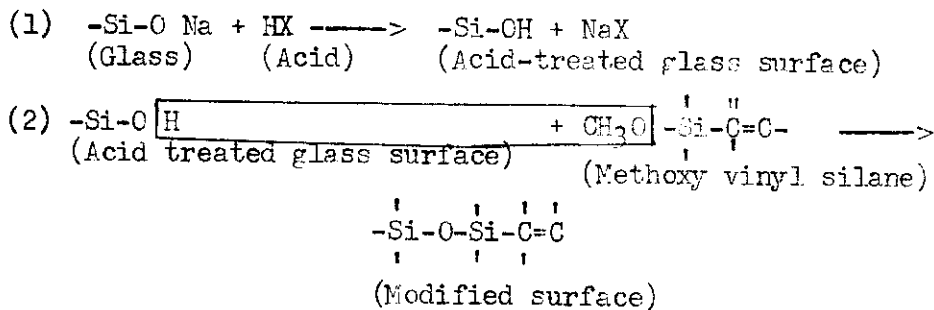


By suitable means of dispersion on fillers, a silicone molecular oriented filler surface is formed which may be represented as follows:



The Si-O part of the silicone molecule becomes firmly bonded to the filler surface and the silicone thus oriented forms a new filler particle surface of tightly-packed, caterpillar, hair-like organic groups. An indication that the bonds between the silicone and the filler surface are chemical as well as physical is the fact that the silicone cannot be removed by solvents in which the silicone is completely miscible. Fillers so treated are said to be completely hydrophobic and have improved dispersion qualities when compounded with organic binders due to the presence of the organic groups which are present on the modified surface.

Another application in which similar principles are applied is found in the treatment of glass fibers to improve the physical properties of reinforced laminates.¹ The glass is first treated with an acid which is believed to induce an abundance of hydroxyl groups on the surface, which make it receptive to an organo-silicone. The organic portion of the organo-silicone contains a group which is capable of reacting with some portion of the organic binder. In the specific example described in the patent cited, a triethoxy vinyl silane was used to form the "bridge". The reactions considered to take place are:



There are numerous other examples of the use of a "bridging" component to obtain a stronger union between unlike substances.

III. Experimental Plan

Based on the background presented above, an experimental plan was formulated to test our theories on the effect of treating the surfaces of filler particles used in dielectric coatings.

Three general classes of binders-phenolics, epoxies and silicones-were selected for investigation. These were selected because of their versatility and the fact that the general technology for using these classes of binders in coatings was well advanced. Two specific, commercially available resins from each general class were chosen to be studied. Five inorganic fillers-glass flake, mica, alumina, silica, and titanium dioxide-were considered in the investigation. Only simple resin-filler coatings were considered in order to eliminate as much as possible the variables which might be introduced by the addition of leveling agents, drying accelerators, anti-skinning agents, ultra-violet stabilizers and other such additives commonly incorporated by coating formulators.

Coating films were prepared from various combinations of binders and fillers. Each film contained only one binder and one filler. These films were tested for water absorption, water vapor permeability, and abrasion resistance. Then, coatings were prepared using fillers which had been surface treated. Three different filler treatments are being investigated. Two of these are heat treatments directed toward removal of foreign

1. U. S. Pat. 2,798,020

material (particularly moisture) from the surface of the particle. One is a mild heat treatment in which the filler is heated at 250° F for 24 hours, allowed to cool in a dry box and incorporated in the resin in a dry box. A more drastic treatment involves heating the filler to a temperature just below sintering under vacuum, allowing to cool and return to atmospheric pressure under nitrogen, and incorporating the filler in the resin in a nitrogen atmosphere.

The use of a chemical bridging agents to effect a stronger bond between the polar surfaces of filler particles and non-polar organic resin was the third filler treatment used. In the work so far, amino-functional silanes have been the only class of compounds tested as bridging agents.

The weight ratio of filler to binder was kept the same for treated and untreated fillers, so that valid comparisons could be made. Using water absorption, water vapor permeability and abrasion resistance as screening tests, the effect of the filler treatment could be judged. The first two tests, water absorption and water vapor permeability, are directly related to the proof of whether or not any of the surface treatments of filler particles improves water resistance. The abrasion resistance test was used to screen the films for general mechanical stability.

The screening tests which are still in progress, should give an indication of the effectiveness of filler surface treatments for the various coating compositions. After the data from the screening tests has been analyzed the most promising coating combinations will be subjected to more extensive mechanical, thermal and dielectric testing. In this area of testing, the effect of vacuum and thermal conditions on the dielectric properties will receive prime consideration. Again the objective will be to ascertain the effect of filler treatment on the physical properties of the coatings.

IV. Results of Experimental Work and Conclusions

Considerable effort was directed toward establishing optimum conditions for preparing films acceptable for testing. It was first necessary to determine empirically the correct grinding conditions necessary to disperse uniformly the filler in each resin filler combination. Films were obtained by doctor-blade and dip-coating techniques depending on the sample requirements of the test.

Moisture vapor transmission tests required free films to be used with standard Gardner Park permeability cups. The results of this test were expressed as transmission-thickness products which appear to be valid for comparing different films which have small thickness differences. Free films applied by doctor-blade or dip-coating were obtained by the tin amalgam technique.

Water absorption was obtained by observing the percent gain in weight which resulted when a supported or free film was immersed in water for a specified length of time.

The resistance to abrasion was determined by a Tabor Abraser apparatus. This apparatus removes material from the surface of the film by means of abrasion wheels. The abrasion resistance was specified by the amount of material removed per 1000 cycles or revolutions of the specimen. Test specimens were prepared by dip-coating standard Tabor abraser panels in the coating mixture.

Early in the program it was discovered that many of the phenolic free films were quite brittle and difficult to handle. Many free films actually cracked so that they could not be obtained in pieces large enough for testing moisture vapor permeability. This was especially true with unfilled phenolics and those in which the fillers were more or less spherical such as silica, alumina, and titanium dioxide. Fillers having a plate-like structure such as glass flake and mica tended to improve the flexibility of the free phenolic films. Some of these films could be handled without cracking, and some water vapor transmission data was obtained.

For example the relationship between water vapor transmission and pigment volume concentration was determined and plotted as shown in Figure 1. It will be observed that the transmission is directly proportional to the pigment volume concentration until a certain critical concentration is reached at which point there is a sharp break in the curve showing a rapid increase in transmission with small increases in pigment volume concentration. The break probably occurs at a point where there is insufficient resin to surround each pigment particle.

In addition to the problem of obtaining flexible free films there was also a problem in obtaining samples of phenolic based coatings on plates for water absorption testing. In many instances, the films partially or entirely failed to adhere to the plate when immersed in water, making it impossible to obtain a value for water absorption.

A method has been described in the literature² for obtaining both water-vapor permeability and water absorption data on coating films supported on glass cloth. In view of the difficulties experienced with phenolic-based coatings as described above, it was decided to investigate the "glass-cloth support" method. Considerable effort was expended in establishing conditions for preparing films supported on glass cloth. The variables considered were the viscosity of the coating mixture, the pigment-volume concentration, drying schedule, and effect of multiple coatings. In the procedure which was adopted the glass-cloth was dipped into the coating mixture and withdrawn at a slow constant speed using a Fisher-Payne Dipcoater. A metal rod was attached horizontally to the bottom of

2. H. F. Payne, "Permeability to Moisture of Organic Surface, Ind and Eng Chem. Anal. Ed 11:453-8 (1939)

the glass cloth to obtain a wrinkle-free coating. Very satisfactory test specimens of phenolic based resins on glass cloth supports were produced using this technique. However, results from the test data indicated that preparation of films on glass cloth introduced new variables which complicated the interpretation of the data.

A. Effects of Viscosity of the Coating Mixture on Water Vapor Transmission

Changes in the viscosity of the coating mixture caused variations in the water-vapor transmission rate of glass-cloth supported films other than those produced by changes in thickness of the film. Higher viscosities apparently do not permit the resin to penetrate into the fibers and coat the individual strands of thread. Therefore, an abnormally high transmission rate-thickness products resulted when the glass cloth was dip-coated with high viscosity coating mixtures. Low viscosities coat the glass cloth with material which is not of sufficient thickness to eliminate the weave pattern from the surface area exposed in the water-vapor transmission test. The exposed fibers will increase the amount of water vapor transmitted. Calculated transmission-thickness products based on the apparent area of the test disk were abnormally high. Only by working with compositions having viscosities within specified limits could these abnormalities be eliminated.

The relationship of film weight (which depends on the viscosity of the coating mixture used for dipping) and the apparent film thickness is shown in Figure 2. This graph shows that the best weight range of coating material for the test disk is between 0.4 and 0.6 gram. In the weight range from 0.2 gram to approximately 0.4 gram, no appreciable change in film thickness occurred. It is in this region that the weave pattern was filled as more resin was deposited with virtually no corresponding increase in apparent film thickness. As more of the resin was deposited, the weave pattern was completely covered, and the thickness showed an increase with greater film weight.

In figures 3 and 4, the film weight was plotted against transmission-thickness product. The lowest transmission-thickness product occurred in the area where the weight of the test disk was in the range of 0.4 to 0.6 gram as explained previously.

B. Water Absorption of Glass Cloth

The water-vapor transmission through an unfilled phenolic resin supported on glass cloth is much greater than through a free film of the same resin. This might be expected because the interface between the surface of the glass fibers and the resin provides a path for the water-vapor molecules to pass through the film.

The amount of water absorbed by the glass cloth and along the glass cloth-phenolic film interface should not be included in the amount absorbed by the coating material. The water absorbed by the glass cloth could not be determined by the standard test because of the difficulty in removing excess water trapped in the interstices of the woven fabric; therefore, an indirect method was devised. For these tests, specimens were prepared using different viscosities of unfilled resin so that different weights of material were deposited on the glass-cloth support. Two phenolic resins were tested in this manner and the weight of water absorbed versus the weight of resin deposited on the glass cloth were plotted. (Figures 5 and 6). The amount of water absorbed by the glass cloth was found by extrapolation to zero weight of resin. The slopes of the curves represent the percentages of water absorbed by the resins.

C. Effect of Bridging Agent on Glass Cloth

Since the data obtained in the preceeding section indicated that the amount of water absorbed by the glass cloth was quite significant, it was desirable to observe the effect of treating glass cloth with a bridging agent. Glass cloth supports, treated with a silicone bridging agent were coated with various amounts of phenolic resin and tested for water-vapor transmission and water absorption. For one of the phenolic resins, Figure 7 shows that the water absorbed by the glass cloth was significantly less than that absorbed by the treated cloth. However, the percentage of water absorbed by the resin was greater for the treated glass cloth than for the untreated cloth. This may be a manifestation of a phenomenon reported by Michael³ who describes an optimum level of bridging material beyond which the properties of the binding resin are deteriorated.

By comparing films of approximately equal weight in figures 3 and 4 the difference in water-vapor transmission of films supported on treated and untreated glass cloth becomes evident. With one phenolic, the water-vapor transmission was improved by using treated cloth; with the other phenolic, no definite conclusions can be drawn because improvement was observed in one only about one-half of the samples in which the glass cloth was treated with bridging agent.

D. Effect of Heating Fillers in Air at Low Temperature and Treating Fillers With a Bridging Agent

Because of the complications which were introduced by the use of glass-cloth supports for phenolic films, it was difficult to evaluate the effect of filler treatment on water absorption and water-vapor transmission. The results so far with glass-flake filler indicate that heat-

3. Michael³, A.S. "Surfactant Treated Minerals as Reinforcing Fillers" Ind & Eng Chem 48, 297-304 (1956)

ing in air at low temperature had little effect on the water absorption or water vapor transmission of phenolic based films.

The treatment of mica and glass-flake filler with a silicone bridging agent did not improve the absorption or transmission of phenolic based films. In some cases there was actually a significant increase in the water absorption of films containing treated filler. Again the effect of the glass-cloth support was a complicating factor making interpretation of results difficult. Treatment of the glass cloth as well as the filler with bridging agent apparently caused both the water absorption and water-vapor permeability to increase.

In the initial phases of our experimental program, we thought that the difficulties encountered in obtaining phenolic free films had been averted by the use of glass-cloth supports. However, the introduction of this variable (glass cloth) caused effects which made it difficult to interpret some of the experimental data on water absorption and water-vapor transmission. Work is now being concentrated on silicone and epoxide-based films which can be obtained readily as free films without the complicating variables introduced by using glass cloth as a support. Later we expect to direct attention toward fabrication of more flexible phenolic free films (possibly by using a plasticizer) to avoid the necessity for using glass cloth as a support.

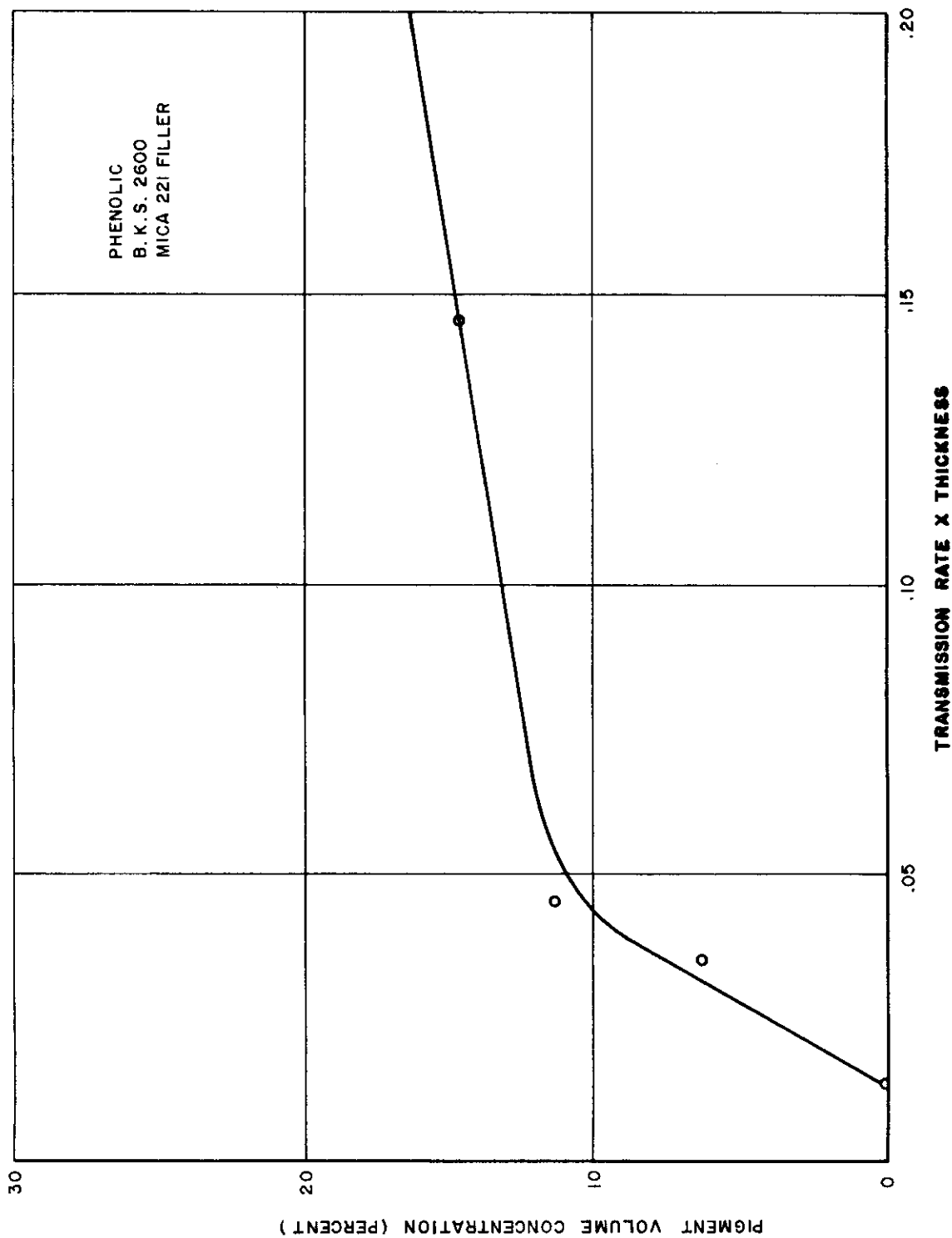


Figure 1. Relationship Between Water-Vapor Transmission and Pigment Volume Concentration of Mica in a Phenolic Free Film

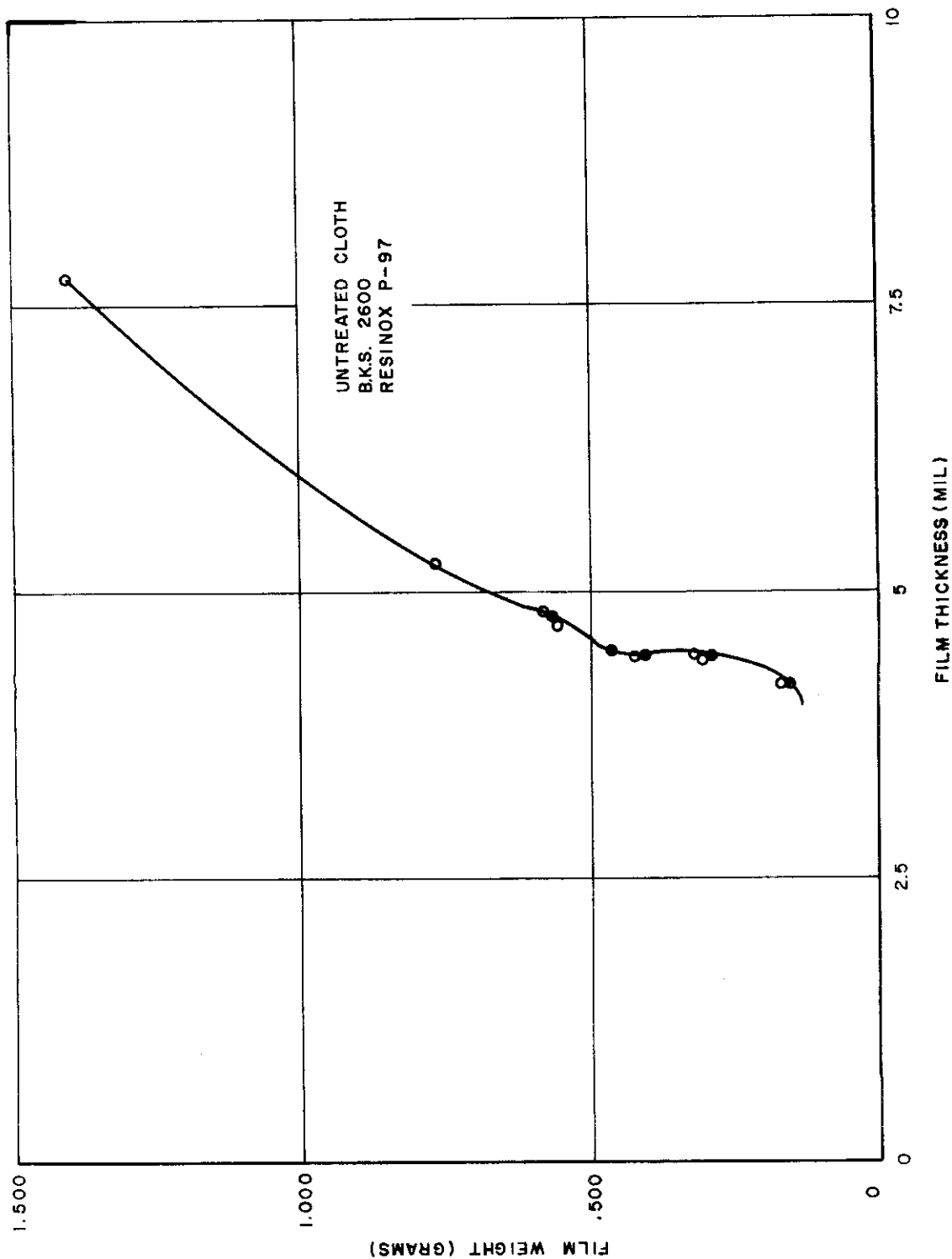


Figure 2. Film Weight vs Film Thickness of Phenolic Resins on Untreated Glass-Cloth Support

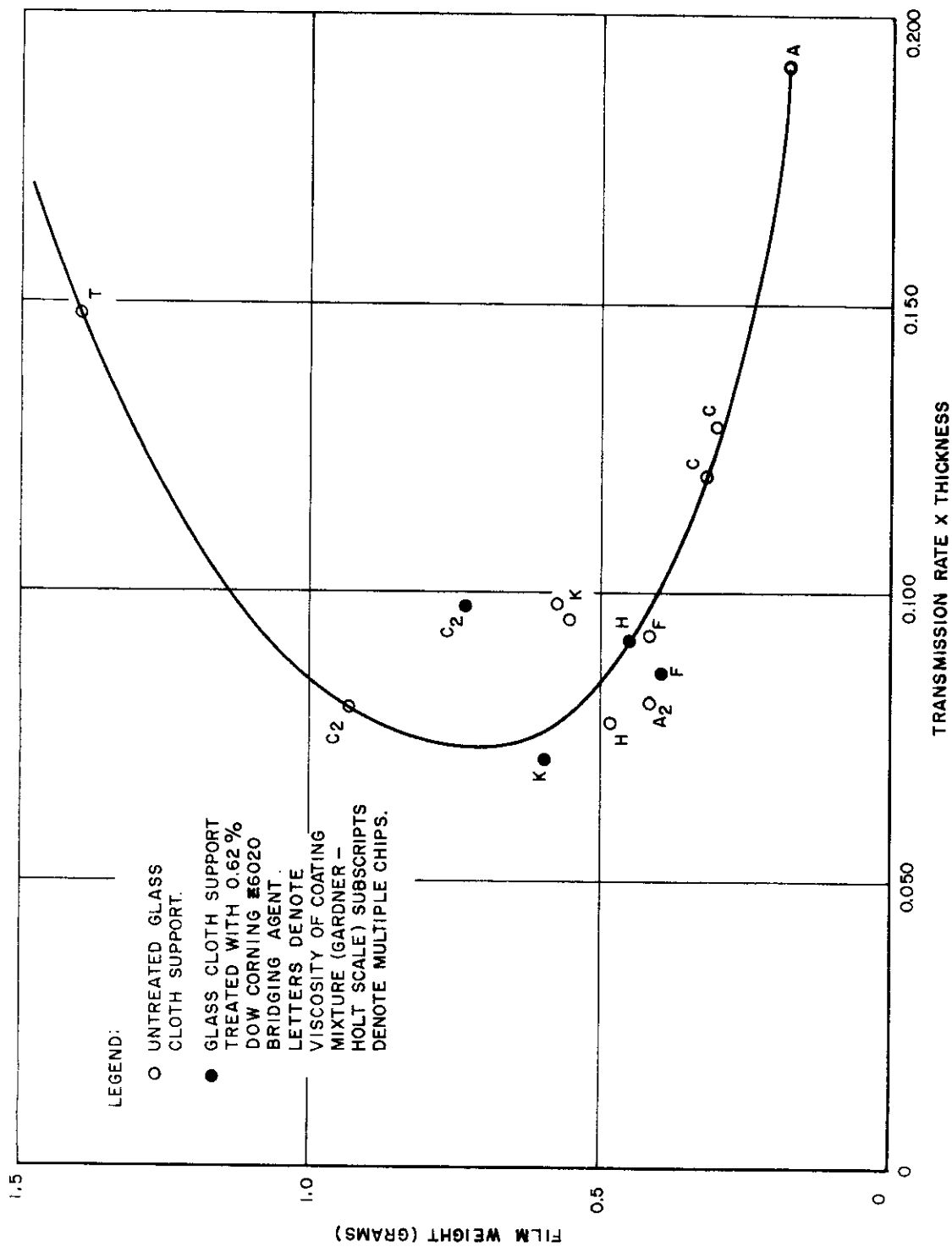


Figure 3. Transmission Rate and Thickness Product vs Film Weight of Phenolic BKS-2600 on Glass Cloth

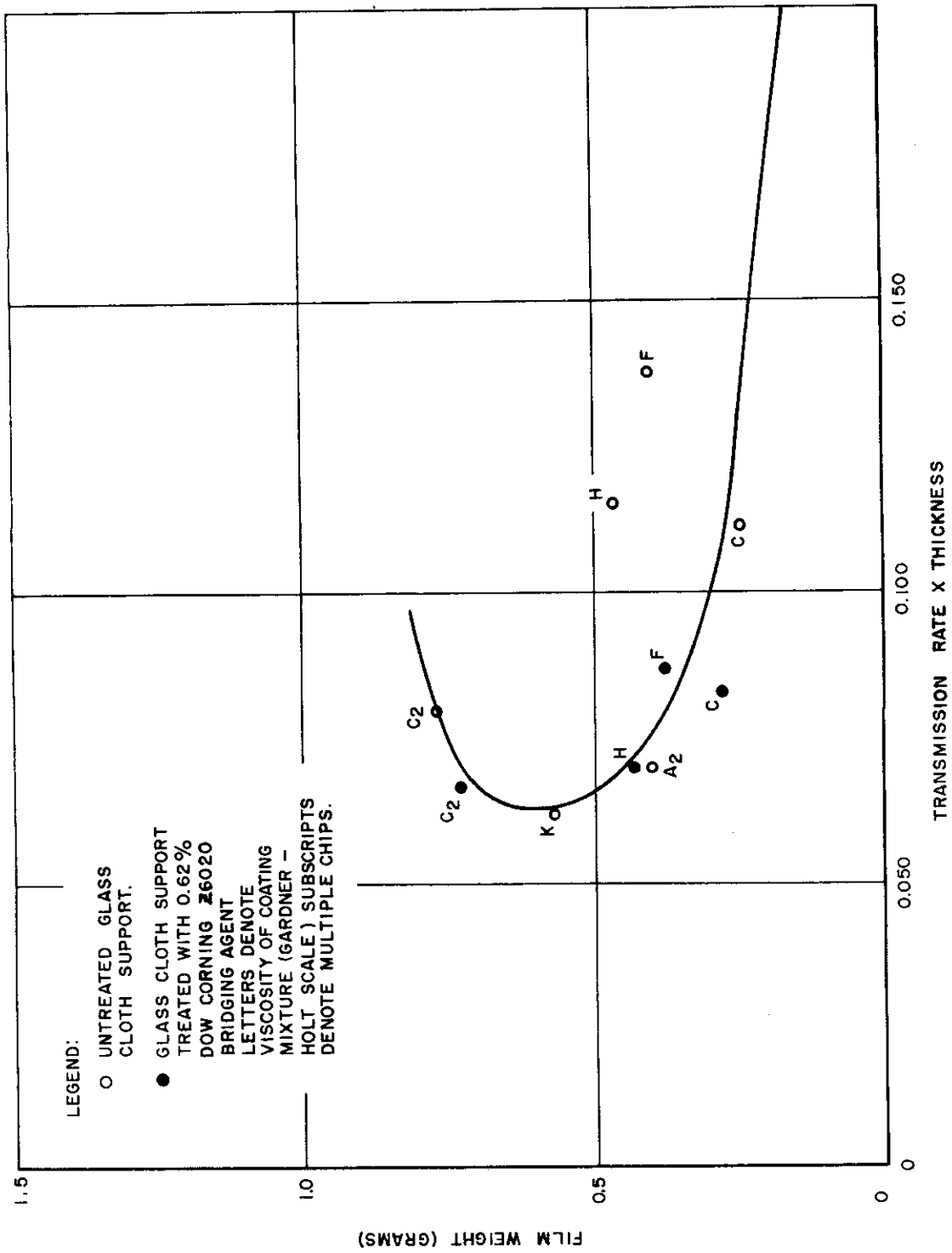


Figure 4. Transmission Rate and Thickness Product vs Film Weight of Phenolic Resinox P-97 on Glass Cloth

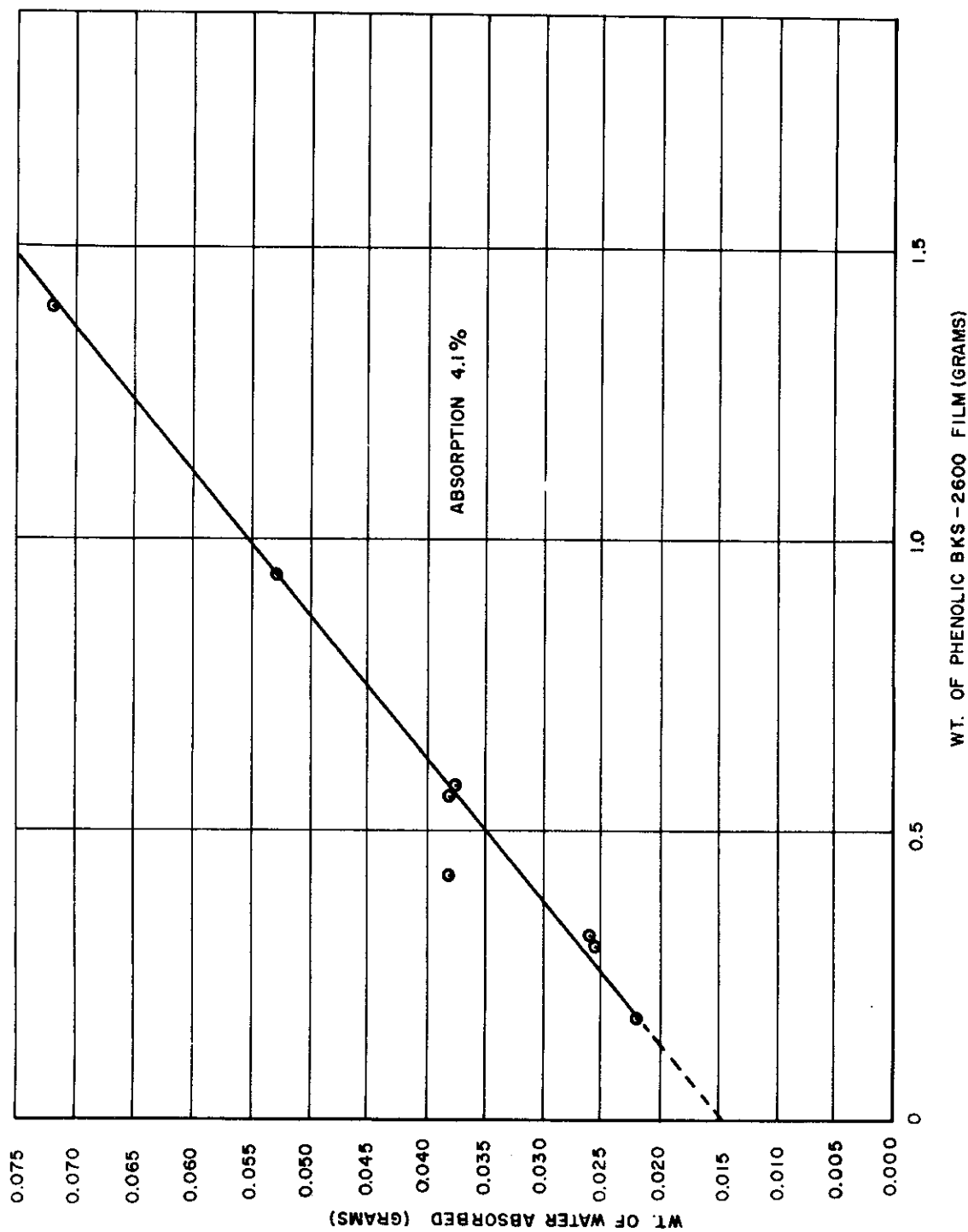


Figure 5. Water Absorption of Phenolic BKS-2600 vs Weight of BKS-2600 on Glass-Cloth Support

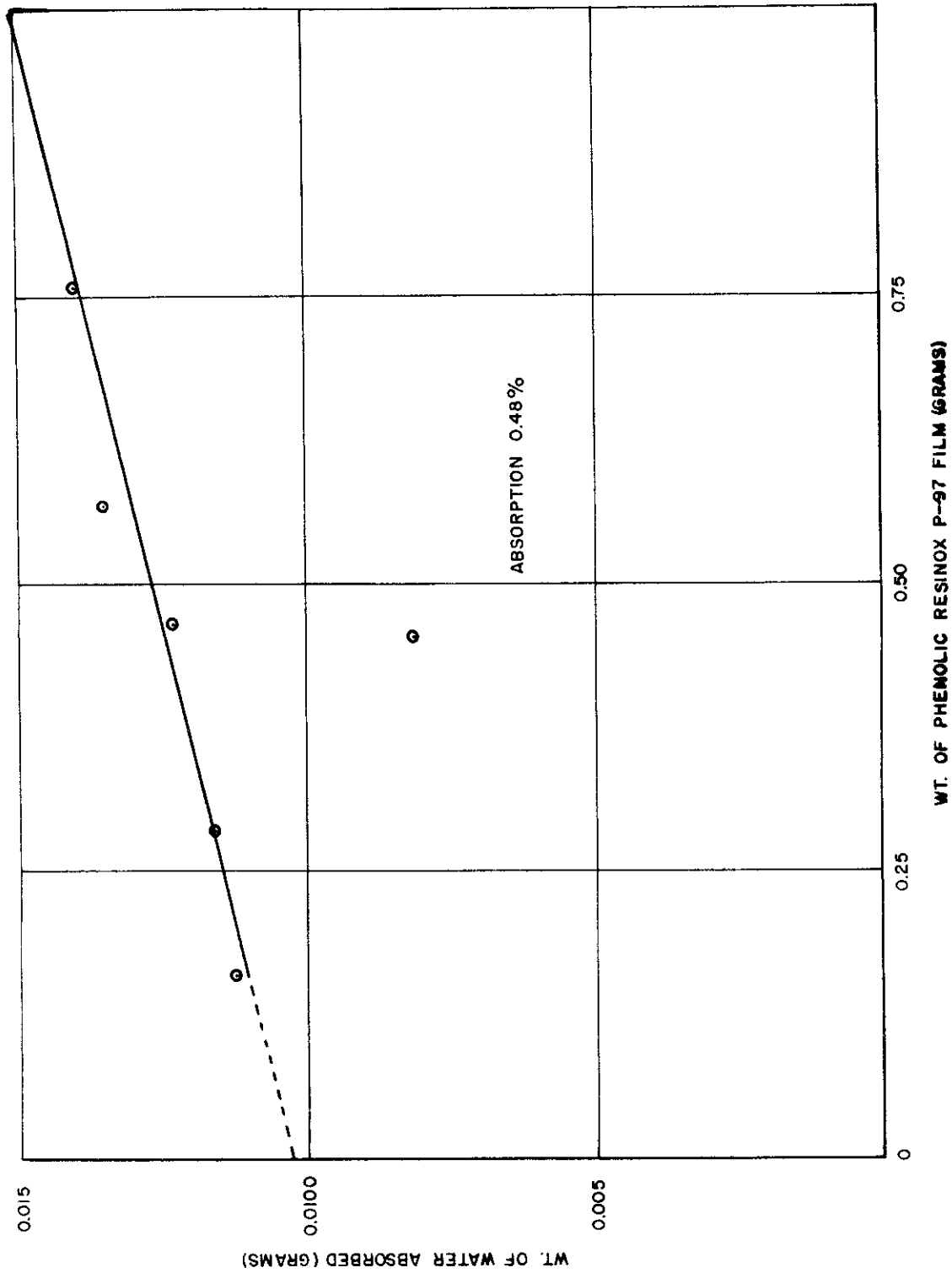


Figure 6. Water Absorption of Phenolic Resinox P-97 vs Weight of Resinox P-97 on Glass-Cloth Support

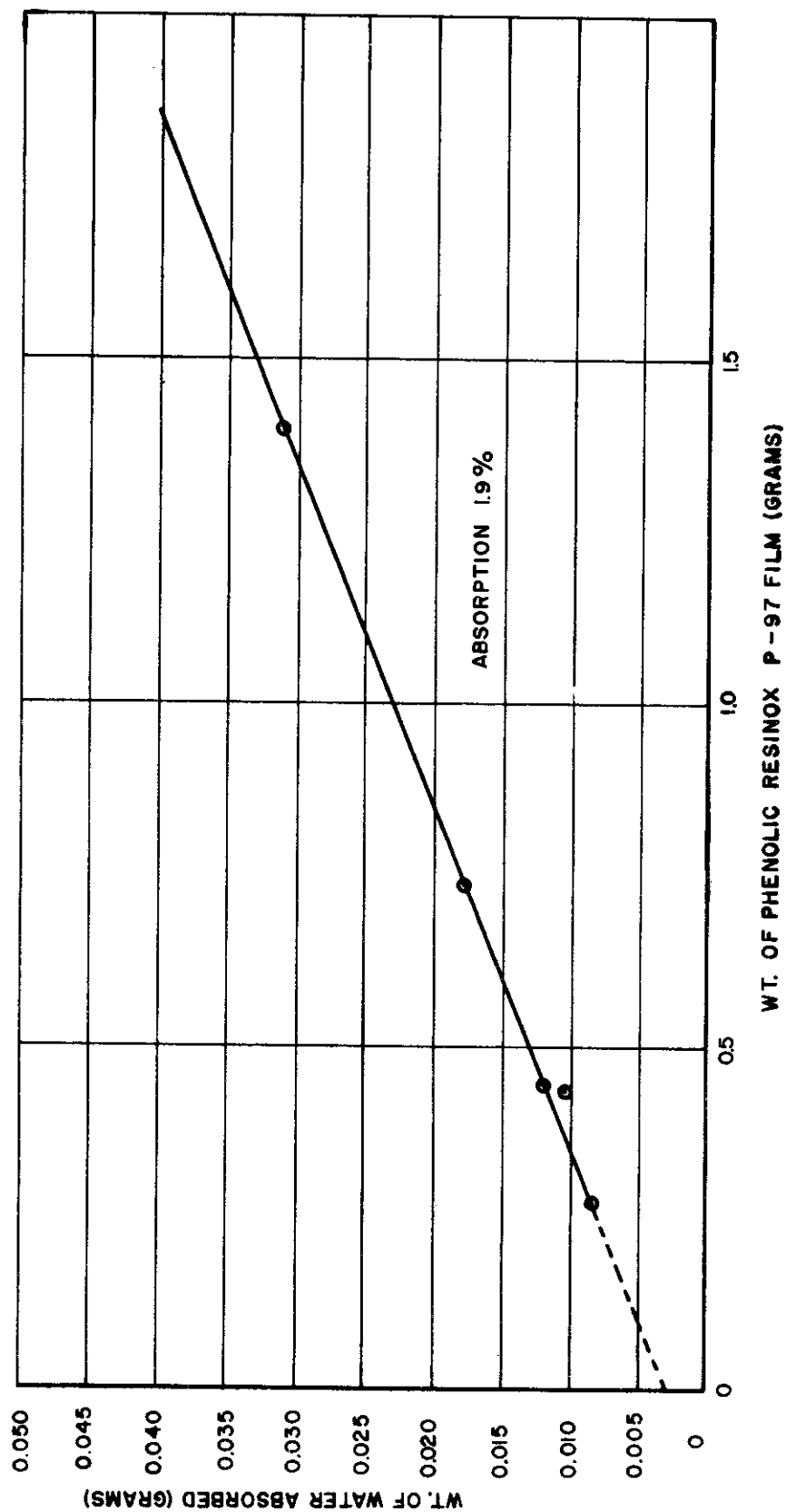


Figure 7. Water Absorption of Phenolic Resinox P-97 vs Weight of Resinox P-97 on Glass Cloth Treated with Dow Corning Z 6020 Bridging Agent

